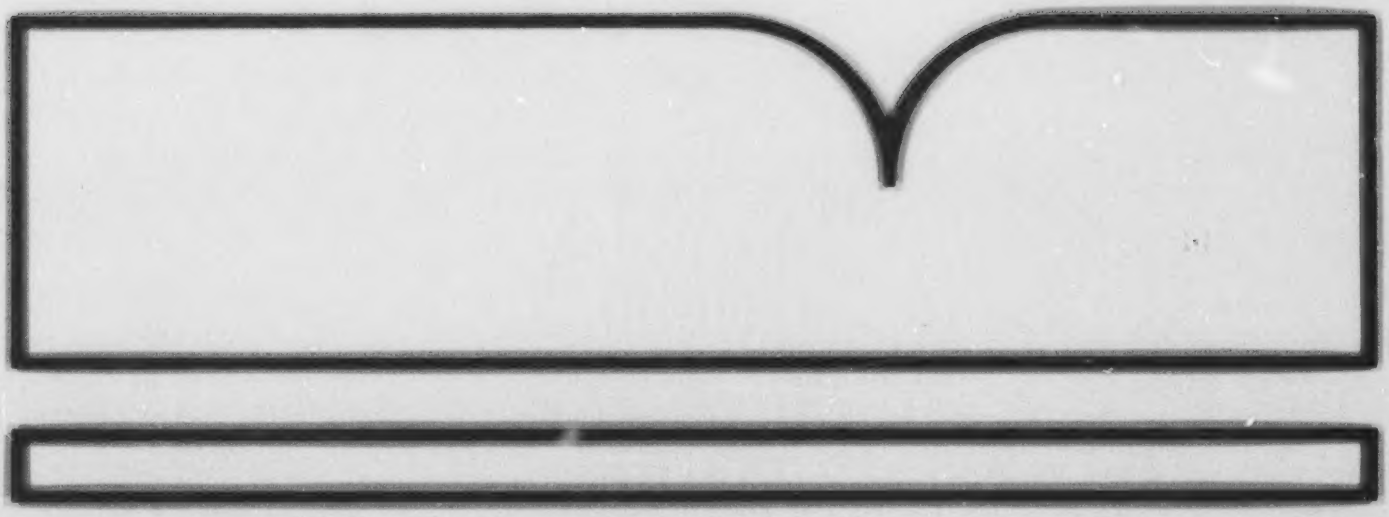
PB88-158795

Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator 2. Contained Liquid Wastes on Sorbent

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

1987



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1. REPORT NO.	2.	3. REC
EPA/600/J-87/166		PB88-158795

4. TITLE AND SUBTITLE	5. REPORT DATE
On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator: II. Contained Liquid Wastes on Sorbent (Journal Version)	1987
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. Linak and J. McSorley (EPA/AEERL), J. Wendt (University of Arizona), and J. Dunn (University of Arkansas)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
See Block 12.	11. CONTRACT/GRANT NO.
	NA (Inhouse)
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development **Air and Energy Engineering Research Laboratory** **Research Triangle Park, NC 27711**	Journal article; 8/86-4/87
	14. SPONSORING AGENCY CODE
	EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is William B. Linak, Mail Drop 65, 919/541-5792. Part I published in JAPCA, 37:1, pp. 54-65, 1/87. Part II published in 37:8, pp. 934-942, 8/87.

16. ABSTRACT The paper gives results of a study of the generation of transient puffs resulting from the batch incineration of liquid waste into a 73 kW rotary kiln incinerator simulator. The liquid was added onto a sorbent, enclosed in cardboard cylinders that are introduced into the combustion chamber one at a time. A statistically designed parametric investigation determined the effects of liquid mass, liquid composition, kiln temperature, and kiln rotation speed on the total magnitude and instantaneous intensity of the pollutant puff leaving the kiln. Liquid wastes investigated included toluene, methylene chloride, carbon tetrachloride, and No. 5 fuel oil. Transient puffs from these wastes were monitored using on-line measurements for FID-measurable hydrocarbons, CO, and integrated particulate filter loadings, although the suitability of any one of these indicators depended on the chemical nature of the waste involved. Study results show that puffs formed during transient conditions are generated easily, even with small quantities of wastes and with the kiln operating at 100% excess air. High kiln temperatures and increased kiln rotation speeds exacerbated the generation of puffs, due to increased liquid evaporation rates. Transient puffs may contain hazardous products of incomplete combustion even though adequate destruction and removal efficiencies are achieved.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Liquids	Pollution Control	13B	07D
Incinerators	Hydrocarbons	Stationary Sources		07C
Kilns	Carbon Monoxide	Transient Puffs	13A	07B
Simulators	Particles	Rotary Kilns	14B	14G
Waste Disposal	Dust	Hazardous Wastes	15E	11G
Toxicity		Liquid Wastes	06T	
		Particulate		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	**Unclassified**	12
	20. SECURITY CLASS (This page) **Unclassified**	22. PRICE PC $9.95 / MF 6-93

EPA Form 2220-1 (9-73)

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EPA/600/J-87/166
JOURNAL ARTICLE

On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator

II. Contained Liquid Wastes on Sorbent

William P. Linak and Joseph A. McSorley
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Jost O. L. Wendt
Department of Chemical Engineering
University of Arizona
Tucson, Arizona

James E. Dunn
Department of Mathematical Sciences
University of Arkansas
Fayetteville, Arkansas

The generation of transient puffs resulting from the batch introduction of liquid waste into a 73 kW (250,000 Btu/h) rotary kiln incinerator simulator was investigated. The liquid was added onto a sorbent, enclosed in cylindrical cardboard containers that were introduced into the combustion chamber one at a time. A statistically designed parametric investigation determined the effects of liquid mass, liquid composition, kiln temperature, and kiln rotation speed on the total magnitude and instantaneous intensity of the pollutant puff leaving the kiln. Liquid "wastes" investigated included toluene, methylene chloride, carbon tetrachloride, and No. 5 fuel oil. Transient puffs from these wastes were monitored using on-line measurements for FID-measurable hydrocarbons, CO, and integrated particulate filter loadings, although the suitability of any one of these indicators depended on the chemical nature of the waste involved.

Results demonstrate that puffs formed during transient conditions are generated easily, even with small quantities of wastes and with the kiln operating at 100 percent excess air. High kiln temperatures and increased kiln rotation speeds exacerbated the generation of puffs, due to increased liquid evaporation rates. Transient puffs may contain hazardous products of incomplete combustion (PICs) even though adequate destruction and removal efficiencies are achieved. Mixtures of chlorinated and nonchlorinated principal organic hazardous constituents (POHCs) in the waste can lead to the formation of more diverse chlorinated compounds than are formed from a single chlorinated POHC such as carbon tetrachloride alone.

This paper is the second of a series. Its companion paper, Part I, which has been published previously,[1] is concerned with solid plastic wastes.

In many practical applications involving the incineration of liquid wastes, combustion of the waste occurs in a batch mode rather than under steady-state conditions. In this batch mode of operation the liquid waste, bound on a sorbent material, is held in containers or drums which are introduced one at a time into the incinerator. Although several incinerator designs capable of handling "containerized" wastes exist, rotary kilns are probably the most common. The sorbent may consist of sawdust, corncobs, or other absorbent material, while the containers (typically drums) may be of cardboard, plastic or metal. Upon entry into the incinerator, the container ruptures or burns, exposing the contents to the hot kiln environment. The liquid then rapidly vaporizes and reacts with the excess oxygen present in the burned gases from the continuous primary flame. A possible kiln failure condition arises when the evolution of waste gases from the sorbent is more rapid than the rate at which the stoichiometric amount of oxygen can be supplied from the primary flame. This transient overchanging condition (unique to batch mode systems) can lead to a "puff" of incompletely destroyed combustible material, which then passes through the entire kiln/afterburner/scrubber incinerator system, and can, under certain circumstances, lead to momentary system failure. The puff may contain not only the principal organic hazardous constituents (POHCs) originally to be destroyed, but also substantial quantities of products of incomplete combustion (PICs) which may be of equal or greater environmental concern.

This paper is the second of a series, describing results of a research pro-

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gram currently under way at the Air and Energy Engineering Research Laboratory of the U.S. Environmental Protection Agency in North Carolina. The overall objectives are directed toward gaining engineering insight into potential problem areas related to rotary kiln incineration. Results pertaining to the the incineration of prototype solid plastic wastes have been reported in Part I of this series.[1] This paper is concerned solely with the generation of puffs arising from the batch introduction of contained liquids on sorbent into a rotary kiln incinerator. Of specific interest is the determination of which liquid waste properties and kiln operating parameters influence the absence or presence of transient puffs. As in Part I, the major concern is only with the generation of puffs in the rotary kiln incinerator itself, and not with the destruction of these transients in an afterburner, nor with their subsequent removal by scrubbers. Rather, this research focuses on the origin and nature of these transients which must subsequently be handled by afterburners and/or pollution control equipment.

The problem is approached through parametric experimentation on the same laboratory-scale rotary kiln incinerator simulator described in Part I. As before, the primary focus is neither on the destruction and removal efficiencies (DREs) of specific POHCs nor on the evaluation of any specific rotary kiln design. Rather, the objective is to delineate, in a generic sense, fundamental combustion phenomena that are important in the formation of transient puffs from liquid wastes and that are worthy of further study. It is hoped that the results presented here will both motivate additional research in this problem area and aid operators and designers of rotary kiln incinerators and afterburner equipment.

Following the organization laid out in Part I, this paper consists of four segments. First, the experimental approach is described and compared to procedures used in the batch incineration of liquids in the field. The second segment contains experimental results from a statistically designed parametric study on the occurrence of puffs from the batch introduction of contained liquids on sorbent. This segment also addresses the problem of how to measure puff magnitude and intensity for a variety of liquid wastes. The third segment is concerned with identification of PICs contained in the puff, and thus, focuses on what must be destroyed in the afterburner downstream. Finally, the fourth segment interprets the results both in the light of important controlling mechanisms and with respect to their implication in the design and operation of kiln/afterburner systems.

Experimental Approach

A detailed description of the EPA rotary kiln incinerator simulator, Figure 1, has been presented in Part I,[1] and therefore, is not presented again in this paper. Part I established that the simulator, although sized at only 73 kW (250,000 Btu/h), was able to exhibit the salient features of practical full-scale units with thermal ratings typically 20 to 40 times larger. In full-scale units, containers are usually charged automatically at a rate of 6–20 per hour, while the rotary kiln simulator required manual charging. In the field, the charge is usually introduced from the burner end of the kiln, and the container slowly travels down the kiln in a co-current fashion. In the simulator, the charge is introduced from the end opposite to the burner and is incinerated in a batch mode. It might be argued that the co-current mode of drum introduction allows entry of some additional air which can travel down the kiln with the drum, that this might help alleviate the occurrence of puffs, and that this phenomenon is not present in the simulator. However, any air that is leaked into the kiln with the charge travels down the kiln at a velocity much greater than that of the waste drum, and is, therefore, unlikely to be near the vaporized liquid when the rupture of the drum allows the waste to enter the surrounding gas phase. Furthermore, the partial pressure of oxygen in the flue gas from the primary flame in the simulator was always in excess of 0.11 atm (11 percent), and it is unlikely that air leakage, which does occur in practice, would substantially alter this. The results presented in this paper have applicability to full-scale units, even though the method of charge introduction is somewhat different.

For the experiments reported here, the kiln was operated under two different thermal conditions. These low fire (1105 K, 1530°F) and high fire (1339 K, 1950°F) conditions resulted in the corresponding temperature profiles shown on Figure 2. These are identical to the temperature profiles used for the previously reported experiments on solid plastic wastes[1] and were accomplished in the same manner. The kiln was always operated at 100 percent excess air with respect to the primary natural gas flame. Kiln rotation speed was varied as a parameter to represent variations in contacting between the waste and its surroundings in the kiln.

For all the experiments reported

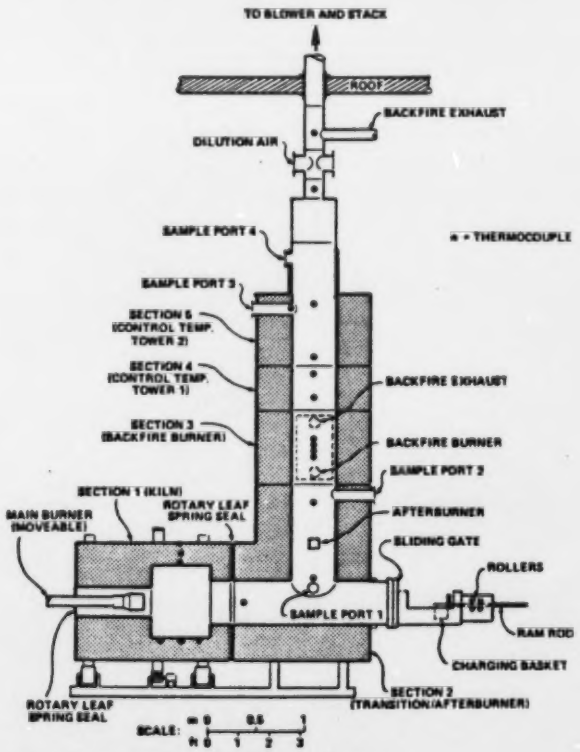

Figure 1. EPA incinerator simulator, cutaway view.

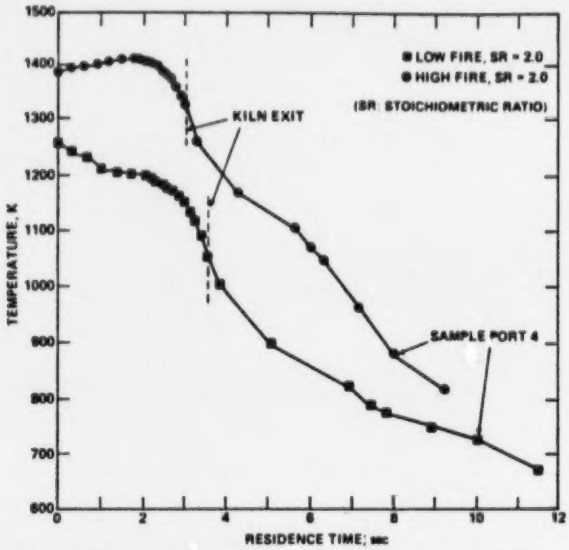

Figure 2. Temperature profile vs. residence time, low and high fire test conditions.

here, the sorbent consisted of 135 g (0.30 lb) of "Slickwick" waste absorbent, composed of ground corncob material manufactured by The Andersons Cob Division, Maumee, Ohio. The sorbent was placed in a cylindrical, closed, quart sized (0.95 L), uncoated cardboard container, 8.9 cm (3.5 in.) in diameter and 16.5 cm (6.5 in.) long. These containers had a tare weight of approximately 45 g (0.10 lb). This combination of container and sorbent was found to give low response (volatile hydrocarbon, CO, and particulate) background blank loadings. Four liquid wastes were chosen as prototypes: toluene, methylene chloride, carbon tetrachloride, and No. 5 fuel oil. These surrogate wastes spanned a range of chemical structures, volatilities, chlorine contents, and stoichiometric oxygen requirements, and represent what might be incinerated in practice.

Each waste sample was prepared in the following manner. The container (including the cardboard lid) and the sorbent were weighed, and a given volume of the liquid waste was introduced onto the sorbent from a measuring burette. The lid was replaced, and the whole assembly was reweighed and then sealed with paper masking tape. Then the sample was incinerated in the rotary kiln simulator. The total elapsed time from introduction of the liquid onto the sorbent to incineration of the container was kept constant at 4 minutes to allow consistent penetration of the liquid into the sorbent.

Real-time sampling and analysis equipment was identical to that described previously in Part I.[1] In addition to real-time total volatile hydrocarbon (THC), CO, CO_2, O_2, and NO_x analyzers, an integrated total filter sample was obtained to provide a measure of carbonaceous particulate loading in the puff. Weighed dessicated quartz filters and the heated particulate filter system upstream of the THC analyzer was used to accomplish this. Total filter weights of the particulate matter collected on the THC filter over the duration of the puff at constant pressure, volumetric flow rate, and temperature (420 K, 300°F) yielded information on relative particulate loadings at different combustion and waste conditions. This method, which should not be confused with EPA method 5, was used to provide a rapid measure of the effects of changes in process variables on relative particulate loadings in the puff. Data from each charge, therefore, consisted of time resolved traces of THC, CO, and the other gases, as well as integrated values of THC and particulates sampled. With the additions noted above, the overall experimental procedure was identical to that reported in Part I and is not reviewed again in this article.

Parametric Studies

The general methodology employed for the experimental design was that of response surface experimentation.[2] This methodology allows one to determine, on the basis of one experiment involving a minimal number of trials, an empirical relationship between the

Table I. Test matrix for liquids on sorbent.

Trial	Rotation	Temperature	Mass	Composition[a]
The first 16 trials test for linear relationships.				
1	1	−1	−1	A
2	−1	1	−1	A
3	−1	−1	1	A
4	1	1	1	A
5	−1	−1	−1	B
6	1	1	−1	B
7	1	−1	1	B
8	−1	1	1	B
9	−1	−1	1	C
10	1	1	1	C
11	1	−1	−1	C
12	−1	1	−1	C
13	1	−1	1	D
14	−1	1	1	D
15	−1	−1	−1	D
16	1	1	−1	D
The next eight trials test for curvalinear (quadratic) trends.				
17	0	1	−1	A
18	0	−1	1	A
19	1	0	1	B
20	−1	0	−1	B
21	1	0	0	C
22	−1	−1	0	C
23	−1	1	1	D
24	1	−1	−1	D

[a] A = toluene; B = No. 5 fuel oil; C = carbon tetrachloride; D = methylene chloride.

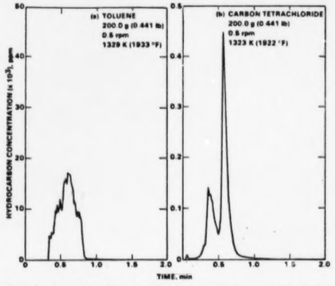

Figure 3. Comparison of toluene and carbon tetrachloride transient hydrocarbon peak shapes at similar trial conditions.

response and the controlled variables in the experimental region. Data on the dependent variables are collected during experimentation at low, intermediate, and high settings of the independent variables. The experimental design used for this study was identical to that used for the prototype solid wastes (see Part I),[1] except that the variable denoting the solid plastic surface area was replaced by kiln rotation speed, for which 0.5 and 2.0 rpm were the low and high values respectively. Rotation speed was chosen because, like surface area for a solid, it directly influences contact between waste/sorbent and the surroundings. The temperature variable was measured at the kiln exit, 0.965 m (38 in.) from the front burner wall. Low and high fire conditions correspond to the two temperature distributions in Figure 2. The following represent the minimum and maximum values for the parametric test matrix:

(a) Kiln rotation speed, 0.5 rpm minimum, 2.0 rpm maximum.

(b) Kiln exit temperature, 1105 K (1530°F) minimum, 1339 K (1950°F) maximum.

(c) Charge mass, 50 g (0.11 lb) minimum, 200 g (0.44 lb) maximum, not including the container and sorbent tare weight of 180 g (0.40 lb).

The following kiln operating parameters were kept constant for all runs reported here:

(a) Auxiliary gas flow rate, 5.66 m^3/h (200 cfh).

(b) Air flow rate, 109.0 m^3/h (3850 cfh), leading to constant stoichiometric ratio (SR) of 2.0 or excess air of 100 percent.

(c) Burner position, −0.34 m (−13.5 in.) inside front burner wall.

(d) Kiln pressure, −37.4 Pa (−0.15 in. H_2O).

(e) Sample port, at position 4 (see Figures 1 and 2).

Table I depicts the experimental test matrix, and the appropriate combination of minimum (−1), maximum (1), and intermediate (0) settings for each trial. The resulting 24 trials allowed quadratic models, as well as full degree of freedom tests of significance of all main effects, and all two-factor interactions,[2] to be formulated.

Each trial consisted of between 5 and 15 replicate charges, and reproducibility was much better for the liquids reported here than for the solids reported in Part I. The total area and peak height of the time resolved traces of total volatile hydrocarbon concentrations (THC), measured by flame ionization detection (FID), were recorded and are hereafter denoted simply as "peak area" and "peak height," respectively. Figure 3 shows typical traces for two different liquids at similar test conditions and demonstrates the significant quantitative and qualitative variations resulting from charge composition. Nonlinearity of the FID response was observed during the most intense puffs (greater than 10,000 ppm of THC).

Quadratic models were fitted to the data, using weighted least squares, where the weights were equal to the number of replicates divided by the sample variance between replicates. These models, obtained using the preprogrammed procedures in SAS (Statistical Analysis System), should not,

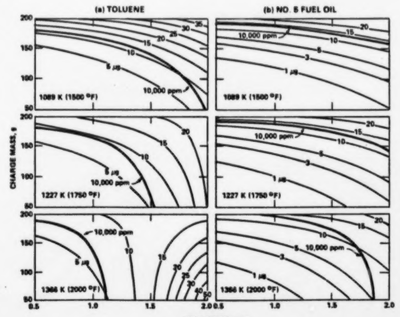

Figure 4. Effect of charge mass, kiln rotation speed, and kiln temperature on the integrated (a) toluene and (b) No. 5 fuel oil hydrocarbon peak area. Contour plots denote total volatile hydrocarbons measured as micrograms of methane.

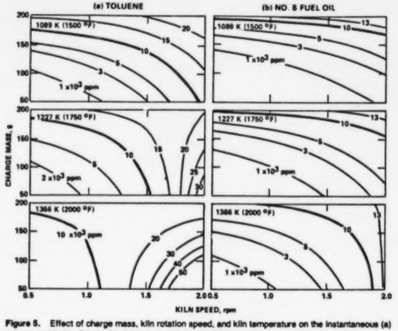

Figure 5. Effect of charge mass, kiln rotation speed, and kiln temperature on the instantaneous (a) toluene and (b) No. 5 fuel oil hydrocarbon peak height. Contour plots denote peak volatile hydrocarbon concentrations measured as parts per million of methane.

however, be considered unique, since other models might attain fits essentially identical to those reported here.

The final response models for peak area accounted for 99.4 percent of the variation in the response caused by changes in parameters, and were of the form:

$$\text{Exp}(\text{Peak area, } \mu\text{g } CH_4) = k1 + aT + bM + cR + d(RM) + e(MT)$$

where T, M, and R are kiln exit temperature, liquid charge mass, and kiln rotation speed, respectively. Only statistically significant dependencies were retained in the model, and peak areas were exponentiated in order to avoid negative values. Coefficients b, c, and d were shown statistically not to vary from waste to waste. Coefficients a, b, and c were positive, but the magnitude of coefficient a depended on the waste. In contrast to the solid plastic results reported in Part I, none of the coefficients changed in sign from waste to waste, indicating greater similarity in behavior among the liquids than was apparent for the plastic samples tested previously.[1]

Quadratic models for peak heights were similar to those for peak area and accounted for 98.9 percent of the variation in the response. Resulting contour plots for peak area and peak height are shown in Figures 4 and 5, respectively. The highlighted curve on Figure 4 represents the 10,000 ppm peak height contour. At the THC concentrations in excess of this value, the FID response was nonlinear leading to true contour gradients that are steeper than those depicted. Toluene results lie on the left of Figures 4 and 5, while those for the fuel oil lie on the right. In all cases, increasing the kiln rotation speed increased the peak area of the FID hydrocarbon trace (Figure 4) and the peak height (Figure 5). This was also true for the two chlorinated liquids. Furthermore, for toluene and fuel oil, both peak area (puff magnitude) and peak height (puff intensity) increased with increasing temperature. This result differs slightly from the solid plastic results reported in Part I, where only puff intensity followed this trend, and it conflicts with the more traditional viewpoint held within the incineration community that high incineration temperatures are always beneficial. This apparent perverse effect of kiln temperature was also observed for methylene chloride, but not for carbon tetrachloride, where results were less definitive.

The saddle contours, apparent for toluene when concentrations of volatile hydrocarbons were very high (lower-left corners of Figures 4 and 5), are anomalous, and cannot be explained by nonlinear response of the FID, since that was found to be monotonic with THC concentration up to 40,000 ppm. A possible explanation for the presence of saddles in these plots is that soot formation is disproportionately accelerated at high hydrocarbon loadings and that, therefore, the remaining volatile hydrocarbons measured by the FID are no longer quantitatively representative of total puff size. Saddles did not appear for the less volatile fuel oil (Figures 4b and 5b) where hydrocarbon loadings were lower. Therefore, we believe that for the less volatile wastes, such as the plastics investigated in Part

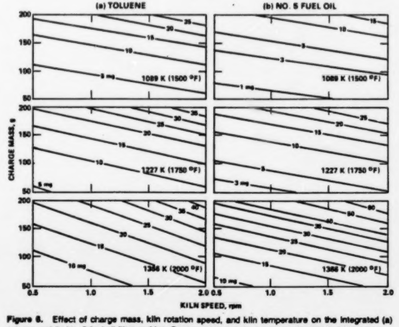

Figure 6. Effect of charge mass, kiln rotation speed, and kiln temperature on the integrated (a) toluene and (b) No. 5 fuel oil filter residue. Contour plots denote particulate loading in milligrams.

Table II. Selected compounds identified in test burns charging toluene and carbon tetrachloride.[a]

	Solvent blank	Baseline[c] (a)	Sorbent/container blank (b)	Toluene (c-1)	Toluene (c-2)	Toluene/carbon tetrachloride[d] (d-1)	Toluene/carbon tetrachloride[d] (d-2)	Carbon tetrachloride (e)
Chlorocyclohexanol	X	X	X	X	X	X	X	X
Phthalate ester	X	X	X	X		X	X	X
Tetrachlorobenzene[b]						X	X	
Pentachlorobenzene[b]						X	X	
Naphthalene				X	X			
Acenaphthalene				X	X			
Anthracene				X	X			
Fluoranthene				X	X			
Pyrene				X	X			

[a] In all cases, the kiln was at high fire conditions (1339 K, 1950°F), 100 percent excess air (SR = 2.0), 0.5 rpm kiln rotation, and 10 charges of 380 g (0.84 lb) each [including 180 g (0.40 lb) container/sorbent], were charged 1 every 10 minutes. Trace quantities of varying chlorinated compounds were identified in all samples including baseline, sorbent/container blank, and toluene samples.

[b] Present in low concentrations in comparison to other listed, but not identified in any other sample.

[c] Baseline test sampled auxiliary fuel combustion gas products, no waste material charged.

[d] Toluene/carbon tetrachloride mix charges were 50 percent each by weight.

I, the FID peak area and peak height contour plots can represent the magnitude and intensity of the puff, provided the hydrocarbon concentrations are not too high.

The similarity between Figure 4, representing contours of integrated measurements, and Figure 5, representing those of instantaneous values, suggests that other integrated measurements, such as that of particulate matter trapped on filters during a puff, should also represent trends in both puff magnitude and puff intensity. Therefore, a statistical analysis was performed on the filter weights recorded for each test. The ensuing model (r^2 = 0.999) contained all the same terms as the peak area model, except for the mass-rotation interaction term. Contour plots for toluene and fuel oil, Figure 6, show conclusively that, as kiln temperature is increased, the total soot loading from the kiln to the afterburner is increased; i.e. a much larger puff is formed. This is significant and again points to potential failure modes if the kiln is operated at too high a temperature.

Filter residue mass contour plots for methylene chloride were qualitatively similar to those shown on Figure 6, but indicated only a slight dependence on kiln temperature. Carbon tetrachloride contour plots for both filter residue and peak area differed sharply from those arising from all the other liquids, and did not lend themselves to physical interpretation. Furthermore, the carbon tetrachloride filter residues were not black and did not resemble soot, while those of the others did. This suggests that, for wastes containing only carbon and chlorine, neither the magnitude nor the intensity of a puff can be determined from measurements of either volatile (FID-measureable) hydrocarbons or integrated filter residue mass. Therefore, we explored the value of using CO peak height as an indication of the presence of puffs, since this has been investigated as a measure of incinerator performance by others.[3-10] Statistical analysis of the data describing maximum peak values of CO allowed a quadratic model, similar to that for FID hydrocarbon peak area, to be formulated, with an r^2 of 0.988. The resulting CO contour plots, for this and all other liquids except toluene, were similar to the FID hydrocarbon peak height plots for fuel oil shown on Figure 5b. This suggests that CO may be useful as a puff indicator for fully chlorinated liquid waste compounds. However, when copious quantities of soot are formed, as was the case for toluene at high kiln temperatures, this indicator ceases to be valid and should not be used alone. In general, no single indicator of puffs exists for all types of wastes, and it is desirable always to monitor at least all three indicators used in this work; i.e., FID-measureable hydrocarbons, CO, and integrated particulate mass. For the wastes considered here it is always possible to choose one or more of these indicators such that physically interpretable contour plots result.

Transient Puff Composition

As in Part I, compositions of the transient puffs from the liquid wastes were determined using VOST (volatile organic sampling train) and SASS (source assessment sampling system) stack sampling trains[11,12] in conjunction with GC/MS analysis.[13] The ability of the kiln without an afterburner to destroy the POHC species adequately as well as to produce PICs was examined. In contrast to our previous work in Part I, however, the PIC analyses were not limited to hazardous compounds defined by RCRA, Appendix VIII.[14] These screening tests were used only for qualitative identification since it was not within the scope of this research to perform exhaustive quantitative chemical analysis.

Results are presented for a solvent blank and for the following test conditions:

(a) A baseline in which the exact procedure for charging was followed, but no charge was entered (i.e., the gate was opened and closed).

(b) A sorbent/container blank in which 10 charges totaling 1.8 kg were used.

(c) Two replicate tests (c-1 and c-2), each involving 10 charges of toluene alone totalling 3.8 kg (including 1.8 kg of sorbent and container).

(d) Two replicate tests (d-1 and d-2), of 50 percent toluene and 50 percent carbon tetrachloride (by weight), each test consisting of 10 charges totalling 3.8 kg (including 1.8 kg of sorbent and container).

(e) One test involving 10 charges of carbon tetrachloride totalling 3.8 kg (including 1.8 kg of sorbent and container).

In all cases, the kiln was operated at high fire conditions (1339 K, 1950°F),

Table III. PCDD and PCDF flue gas concentrations determined from test burns charging toluene and carbon tetrachloride. Average flue gas concentration, ppt (volume).

	Solvent blank	Baseline (a)	Sorbent/ container blank (b)	Toluene (c-1)	Toluene (c-2)	Toluene/ carbon tetrachloride (d-1)	Toluene/ carbon tetrachloride (d-2)	Carbon tetra-chloride (e)
Mono-CDD						—[a]	—	—
Di-CDD						—	—	—
Tri-CDD	N	N	N	N	N	—	—	—
Tetra-CDD	O	O	O	O	O	1.3	1.8	0.9
Penta-CDD	N	N	N	N	N	1.3	2.5	—
Hexa-CDD	E	E	E	E	E	0.8	1.7	—
Hepta-CDD						—	0.7	—
Octa-CDD						—	0.2	0.6
Mono-CDF	D	D	D	D	D	—	—	—
Di-CDF	E	E	E	E	E	—	—	—
Tri-CDF	T	T	T	T	T	—	—	—
Tetra-CDF	E	E	E	E	E	14.1	8.4	0.9
Penta-CDF	C	C	C	C	C	16.9	21.5	0.7
Hexa-CDF	T	T	T	T	T	7.7	12.9	0.7
Hepta-CDF	E	E	E	E	E	1.2	2.5	0.8
Octa-CDF	D	D	D	D	D	—	0.2	1.8

[a] Not detected.

with 100 percent excess air, and the charges were introduced at a rate of one every 10 minutes.

The VOST results show benzene and toluene to be present for all of the tests including the baseline test (a), and carbon tetrachloride to be present in both the toluene/carbon tetrachloride (d-1 and d-2) and carbon tetrachloride (e) tests. DRE calculations, however, indicate adequate destruction of the POHC species in excess of 99.99 percent. Particulate loadings, however, determined by SASS filter weights averaged over the entire 100 min test, exceeded the RCRA regulated limit of 180 mg/dscm (0.08 gr/dscf, corrected to 7 percent O_2)[14] for all samples except the baseline (a), sorbent/container blank (b), and carbon tetrachloride (e) experiments. The toluene (c-1 and c-2) and toluene/carbon tetrachloride (d-1 and d-2) tests exceeded the particulate limit by as much as a factor of nine.

Extracted and concentrated samples from all parts of the SASS train were combined. Table II presents a selected list of major peaks identified by GC/MS analysis. The data show contaminant phthalate ester and chlorocyclohexanol species present in all the samples, including the baseline (a) and sorbent/container blank (b). Of interest is the detection of several polycyclic aromatic hydrocarbons (PAHs) (acenaphthalene, anthracene, fluoranthene, and pyrene) in the toluene samples (c-1 and c-2) but not in the toluene/carbon tetrachloride mix (d-1 and d-2) or carbon tetrachloride (e) samples. In addition, low concentrations of tetra and pentachlorobenzene were detected in the toluene/carbon tetrachloride mix samples (d-1 and d-2), but not in any of the other samples. The carbon tetrachloride (e) sample was found to be free of both the chlorinated benzene and PAH compounds. These results are consistent with the transient results presented in the previous sections of this paper and with the results from Part I, and are discussed further below. Note that trace quantities of various chlorinated compounds were identified in all the samples including the baseline, blank, and toluene samples, but the source of these compounds is most likely residual contamination of the kiln refractory, sampling system, and/or the analytical instruments.

Samples were also quantitatively analyzed for polychlorinated paradibenzo dioxins (PCDDs) and polychlorinated paradibenzo furans (PCDFs). GC/MS with selected ion monitoring was employed on concentrated samples. Table III summarizes the integrated concentrations of PCDD and PCDF species identified in these flue gas samples. No PCDDs or PCDFs were detected in the solvent blank, baseline (a), sorbent/container blank (b), or toluene (c-1 and c-2) samples. Both the toluene/carbon tetrachloride mix (d-1 and d-2) and the carbon tetrachloride (e) samples contain parts per trillion concentrations of tetrachloro through octachloro dioxins and furans. The carbon tetrachloride sample (e) contained substantially less PCDDs and PCDFs than did the toluene/carbon tetrachloride mix samples (d-1 and d-2). It should be emphasized, however, that any flue gas concentrations are integrated averages of values that are not constant over the 100 minute sampling period. Furthermore, it must be restated that all of these samples represent effluent from the kiln prior to the afterburner and therefore describe what must be destroyed by the afterburner or removed downstream.

Discussion

This section discusses the interpretation of the data in light of chemical and physical phenomena occurring inside the kiln and how these phenomena might influence the ability of afterburners and scrubbers to minimize total transient emissions. The two most significant findings are: 1) puffs are created very easily, at both low liquid loadings and high excess air values; and 2) high kiln temperatures tend to exacerbate the formation of puffs, at least from hydrocarbon liquid wastes. In order to explore these facets in greater detail, additional experimental runs were performed to allow the effects of charge mass and kiln temperature to be determined by changing each of these variables one at a time. Of specific interest was to determine if and when a "threshold" charge mass existed at which value puffs would suddenly appear.

Results shown in Figure 7, in which FID-measurable hydrocarbon peak area and integrated filter residue weight are shown as a function of liquid charge mass and kiln temperature. The liquid waste was toluene with sorbent and container masses as before. The kiln was operated at 100 percent excess air, 0.5 rpm, and the two temperatures corresponding to low and high fire conditions (Figure 2). Open symbols correspond to low fire, low kiln temperatures, and shaded symbols to high fire, high kiln temperatures. A low kiln rotation speed (0.5 rpm) was chosen in or-

der to minimize regions of nonlinear FID response. Although there is appreciable scatter, these additional results are completely in line with those from the statistical experimentation. Puffs arise at toluene charge mass values less than 30 g (0.066 lb). Peak area data for toluene at high temperatures (Figure 7a) demonstrate little effect of charge mass, as demonstrated by the lack of contours on the left-hand side of the lower portion of Figure 4a. Again, we believe this results from nonlinear FID response and from soot formation. Filter loading data (Figure 7b) conclusively show that, at higher kiln temperatures, more particulate matter is formed in the kiln and that high kiln temperatures can exacerbate puff formation. The practical inference to be drawn is that high kiln temperatures will make greater demands on the afterburner downstream in order to destroy the puff completely.

A significant waste property determining the magnitude of the puff is, as expected, the stoichiometric oxygen requirement of the liquid waste. This result is similar to our previous result for solid plastic wastes as reported in Part I.[1] As in the case of chlorinated plastics (PVC), the chlorinated liquids yielded smaller puffs than the non-chlorinated hydrocarbon wastes, in part because of their lower oxygen demand.

As in Part I, puffs consist of toxic secondary combustion products (PICs). Chlorinated PIC compounds are more likely to be formed when mixtures of dissimilar materials such as toluene and carbon tetrachloride are burned, than when the latter is burned alone. Carbon tetrachloride forms relatively small puffs. Excess oxygen is neither totally depleted nor displaced, even though large quantities of chlorine are present, few chlorinated PICs are formed. Toluene alone, on the other hand, a known soot precursor, forms intense puffs of great magnitude. Excess oxygen is much more extensively depleted or displaced, and although no chlorine is present to allow the formation of chlorinated PICs, there is a propensity to form large quantities of soot and associated PAH compounds. Toluene/carbon tetrachloride mixtures provide both the necessary chlorine and pyrolytic conditions to promote chlorinated PICs. Therefore, carbon tetrachloride alone may not be the most suitable surrogate compound to investigate the formation of PICs, at least in the transient mode. These conclusions are analogous to those reached in Part I with respect to the compositions of puffs from polyethylene/polyvinylchloride mixtures compared to those from polyvinylchloride alone.

The thermodynamic stability of certain chlorinated compounds, including TCDD (thermochemistry from Tsang and Shaub[18]), was investigated for a wide range of local stoichiometries likely to be valid in the puff. Multicomponent equilibrium calculations, involving 33 species, indicated that very fuel rich conditions possibly encountered in the puff could create thermodynamically stable trace quantities of CH_2Cl_2, CH_3Cl, and COCl, but that predicted TCDD mole fractions were always less than 10^{-19}. The levels of TCDD compounds measured in this work are above equilibrium concentrations for all possible conditions in the puff; therefore, their formation is likely to be kinetically, rather than equilibrium, controlled.

Fundamental mechanisms governing the generation of puffs for plastic wastes are different than those for liquid wastes on sorbents. For the former, the volatile release rate depended on the rate of pyrolysis of the plastic, and this could be correlated with differential thermogravimetric analyses. For liquid wastes on sorbents, thermogravimetric analysis showed no interesting distinguishing features between wastes and therefore could not be related to the contour plots describing the transients. Rather, the volatile release rate is most probably controlled by heat transfer to and simple evaporation from the sorbent, and the surface exposure of the sorbent to the surroundings. If this hypothesis is correct, then the important waste parameters for liquid wastes would be their normal boiling points and their latent heats of vaporization. One might further hypothesize that surface exposure of the sorbent is increased as kiln rotation speed is increased. This hypothesis is consistent with all the data presented here, which indicate that both puff magnitude and

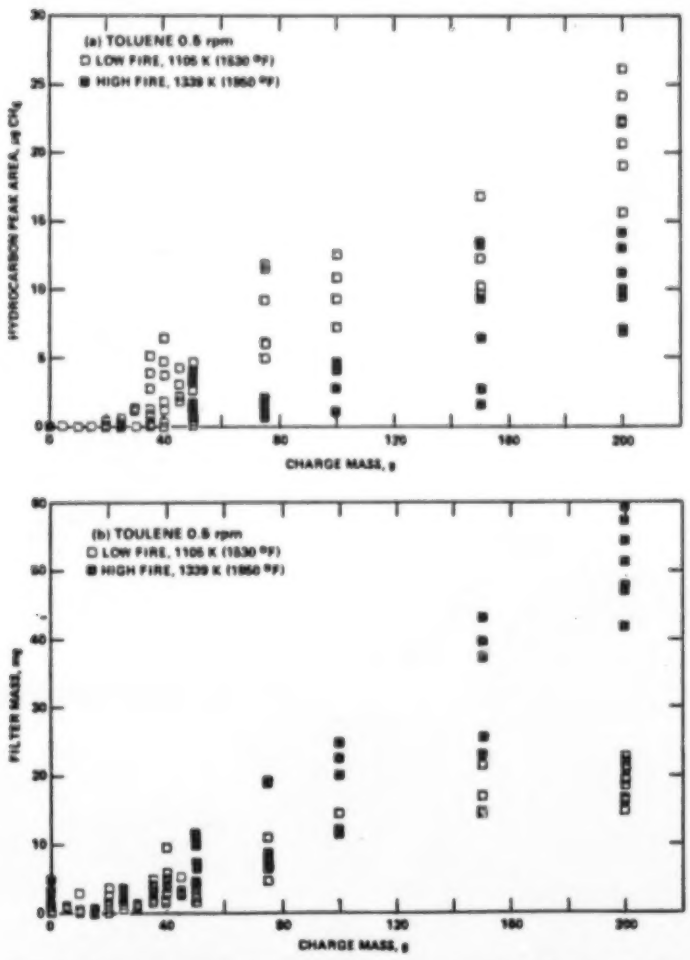
(a) TOLUENE 0.5 rpm
LOW FIRE, 1105 K (1530 °F)
HIGH FIRE, 1339 K (1950 °F)
HYDROCARBON PEAK AREA, pA CH4
CHARGE MASS, g
(b) TOLUENE 0.5 rpm
LOW FIRE, 1105 K (1530 °F)
HIGH FIRE, 1339 K (1950 °F)
FILTER MASS, mg
CHARGE MASS, g

Figure 7. Data showing effect of charge mass and kiln temperature on the integrated toluene (a) hydrocarbon peak area and (b) filter residue. Kiln rotation speed kept constant at 0.5 rpm.

intensity increase with increasing kiln speed. Work is in progress to test these hypotheses using phenomenological models.

Time resolved measurement of puffs is not trivial. Volatile hydrocarbons give a fair indication when levels are not too high; i.e., at low to moderate volatile release rates, as for fuel oil or plastics. Filter residue mass was a better indicator for toluene, when black particulate matter appeared to be the prime constituent of a puff. Neither of the above was suitable for carbon tetrachloride waste, for which CO appeared to be the better on-line indicator. However, CO was a poor indicator for toluene. Therefore, we conclude that no single on-line measurement is suitable for all liquid wastes, and that the omission of any one of the indicators used here might lead to error. However, simultaneous measurement of volatile hydrocarbons, filter residue, CO, CO_2, O_2, and NO_x as puff indicators appears to span the waste conditions encountered in this study.

Conclusions

A laboratory rotary kiln incinerator simulator yielded useful information about how kiln operating parameters and waste properties influence the generation of transient overcharging conditions during the batch introduction of liquid wastes on sorbent held in cardboard containers. These puffs are very easily generated and contain toxic products of incomplete combustion, even though required DREs are achieved easily. The research presented here has important implications in the design of afterburners, since the data indicate that the afterburner plays a crucial role in an incineration system operated in batch mode. The kiln serves essentially to devolatilize the waste into the gas phase, and complete oxidation in the kiln will not occur even at very high primary flame excess air values (SR = 2.0). High kiln temperatures and high kiln rotation speeds increase volatile release rates and increase the magnitude and intensity of the puff, placing additional demands on the afterburner. In general, increasing charge mass increases transient emissions. No single on-line measurement was suitable for all the wastes examined, and omission of any one indicator may lead to error. However, simultaneous measurement of volatile hydrocarbon concentration, filter residue mass, CO, CO_2, O_2, and NO_x as puff indicators appears to span the waste conditions encountered in this study. In addition, the importance of integrated indicators is illustrated.

Acknowledgments

The authors would like to thank EPA/AEERL's R. W. Lowans, R. A. Grote, N. L. Butts, and R. B. Perry for their technical advice and assistance in the construction and data collection phases of this project. Special thanks to R. E. Hall, Branch Chief, Combustion Research Branch, AEERL, for his guidance and support. We would also like to thank the EPA's Hazardous Waste Engineering Research Laboratory (HWERL) for partial support of this work.

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The research described in this article has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Dr. Linak and Mr. McSorley are project officers with the Air and Energy Engineering Research Laboratory, MD-65, U.S. EPA, Research Triangle Park, NC 27711. Dr. Wendt is a professor of Chemical Engineering at the University of Arizona, Tucson, AZ 85721. Dr. Dunn is a professor of Mathematical Sciences at the University of Arkansas, Fayetteville, AR 72701. This work is part of an ongoing EPA in-house research program conducted at EPA's Air and Energy Engineering Research Laboratory, at Research Triangle Park, examining the combustion characteristics of hazardous waste incineration.

This manuscript was submitted for peer review April 23, 1987; the revised manuscript was received June 19, 1987.

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